

PATENT SPECIFICATION

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(54) TREATMENT OF COPPER IRON SULFIDES

(71) We, PENNZOIL COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of, 900 Southwest Tower, Houston, Texas, 77002, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates generally to hydrometallurgical processes for the production of metallic copper from copper iron sulfide ore concentrates. In particular, this invention is concerned with the treatment of copper iron sulfides to make the sulfides more responsive to hydrometallurgical processing. In accordance with this invention, chalcopyrite and other copper iron sulfides are reacted with sulfur vapor to transform these sulfides into other compounds which can be more easily leached.

In recent years the public and governmental agencies have become increasingly concerned with the degradation of the environment. In the western part of the United States copper smelters which process copper ore concentrates are regarded as one of the major sources of air pollution. These smelters emit gaseous streams containing particulate matter and sulfur oxides.

Sulfur oxides, which have been found very difficult to control, result from the smelting of sulfur-bearing ores. Although copper exists in various other forms in nature, such as native copper and copper oxides, carbonates and silicates, the primary sources of copper exist as low-grade deposits of copper iron sulfide ores, with the principal copper mineral being chalcopyrite.

Instead of trying to control the emissions of air contaminants, such as sulfur oxides, once they are formed, hydrometallurgical processes offer an alternative approach by avoiding the formation of the air contaminants. It has been recognized for some time that in the leaching of copper sulfide minerals, the sulfur can be recovered in solid elemental form. This is in contrast to present smelting or pyrometallurgical processes where the sulfur is removed by oxidizing the minerals at elevated temperatures, thereby forming sulfur oxides.

At the present time in the copper industry, hydrometallurgy is generally restricted to the treatment of the more easily leached copper oxide ores and native copper deposits. Aside from waste-dump leaching in copper sulfide mining operations, hydrometallurgy has not been generally applied to sulfide minerals on a commercial scale. In these limited applications of hydrometallurgy, the most commonly used lixiviants are sulfuric acid and ferric sulfates.

Of the copper sulfide minerals, chalcopyrite, which is the principal copper mineral in the United States, has been found to be the most resistant to treatment by hydrometallurgical processes. Processes developed for the treatment of chalcopyrite have been plagued with low recoveries of copper from the ore. Some processes have been able to recover a substantial amount of the copper in the ore but only after the leaching operation has been carried on for a number of hours which is economically undesirable. A further problem in the processing of copper iron sulfide ores is the simultaneous dissolution of the iron which acts as a contaminant in the copper recovery steps.

One attempt to make the copper iron sulfides more responsive to hydrometallurgical processes is disclosed in Vizsolyi et al, United States Patent No. 3,459,535 (1969). Although the process disclosed in the Vizsolyi patent results in improved copper recovery in shorter periods of time, it does not seem amenable to

commercial utilization in view of the batch operation, relatively long reaction time, material handling difficulties and failure to achieve high copper recoveries in shorter periods of time.

5 It has been discovered that the difficulties of prior art processes can be obviated by treating copper iron sulfide ore concentrates with sulfur vapor, thereby forming other copper iron sulfides which can be more easily leached by conventional leaching agents, such as sulfuric acid-oxygen solutions, sulfuric acid-ferric sulfate solutions, and ferric chloride and/or cupric chloride solutions. This sulfidizing process, which takes as little as 6 minutes to complete, is preferably
10 operated at a temperature in the range from 460°C. to 500°C. and at a sulfur vapor partial pressure from 200 mm of Hg to 760 mm of Hg.

In treating chalcopyrite as described, the primary product has been identified by x-ray diffraction as x-bornite. Under certain reaction conditions idaite (usually designated as Cu_3FeS_4) has been formed. One of the discoveries of this invention
15 has been the development of a commercial process for the production of these two relatively rare minerals.

The main advantage in reacting the ore concentrate with sulfur vapor instead of liquid sulfur is the physical form of the product. When utilizing sulfur vapor the product is in a granular or powder form, while lumps or other large pieces of
20 product are formed when liquid sulfur is used as the starting material. The formation of a granular product which can be readily leached without further treatment enables the sulfidizing process to be used on a continuous basis. On the other hand, the formation of relatively large pieces of product when the ore concentrate is reacted with liquid sulfur limits the practicality of the process.
25 These large pieces tend to stick to the sides of the container and are difficult to remove. Furthermore, they must be ground to a fine particle size before they can be effectively leached within a relatively short period of time.

It has been found that by treating chalcopyrite with sulfur vapor as much as 98.5% of the copper in the chalcopyrite can be recovered by leaching with sulfuric acid-oxygen solutions in as little as two hours. If a ferric chloride and cupric
30 chloride solution is used as the lixiviant, leaching tests have shown that as much as 98.8% of the copper goes into solution in as little as 15 minutes. Moreover, during the leaching of the reaction product from the sulfidizing process very little of the iron present as pyrite is attacked by the leaching solution, regardless whether a sulfate or a chloride solution is used.
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In seeking to maximize the copper recovery, it has been found that pyrite crystals frequently prevent the copper iron sulfide from being fully exposed to the leaching solution, thus preventing solubilization of the copper in the sulfide material. To increase copper recoveries to greater than 99%, it has been
40 discovered that grinding the residue from the initial leaching of the x-bornite or idaite to a particle size of at least about minus 200 mesh "cracks" away from the pyrite crystals, thereby exposing the remaining copper iron sulfides to the leaching solution.

The present invention provides a method of processing copper iron sulfide ore concentrates for the hydrometallurgical production of metallic copper wherein the
45 ore concentrates are leached to solubilize the copper, comprising the step of making the copper iron sulfides in the ore concentrates more responsive to the leaching by reacting sulfur vapor having a partial pressure of at least 200 mm Hg with the ore concentrates at a temperature of from 440°C. to 530°C. for a period
50 of at least 6 minutes.

The present invention also provides a method of processing copper iron sulfide ore concentrates for the hydrometallurgical production of metallic copper, comprising the steps of solubilizing substantially all of the copper in the copper iron sulfides by:

55 (a) reacting sulfur vapor having a partial pressure of at least 200 mm Hg with the ore concentrates at a temperature of from 440°C. to 530°C. for a period of at least 6 minutes to form a reaction product consisting principally of copper containing material and pyrite;

60 (b) leaching the reaction product from step (a) to solubilize most of the copper in the reaction product;

(c) grinding the solid residue from step (b) to a particle size of less than 200 mesh (U.S. standard sieve); and

(d) leaching the ground residue from step (c) to solubilize substantially all the remaining copper in the reaction product.

Detailed features of the invention will become apparent from the following description and with reference to the accompanying drawings in which:

Figure 1 is a section view of a reactor that can be used in accordance with the present invention for the sulfidizing of copper iron sulfide ore concentrates.

Figure 2 is a top view of the reaction chamber plates in the reactor of Figure 1.

Figure 3 is a graph showing the relationship between the reaction temperature and the chalcopyrite conversion for various partial pressures of sulfur in the sulfidizing of chalcopyrite ore concentrates.

Figure 4 is a graph showing the optimum residence times in the sulfidizing of the chalcopyrite ore concentrates.

Figure 5 is a graph showing the present copper extracted by sulfuric acid leaching for x-bornite and idaite as compared to non-sulfidized copper-containing materials.

Figure 6 is a flow sheet of the process of this invention for the production of metallic copper from chalcopyrite ore concentrates utilizing sulfuric acid as the leaching agent.

In accordance with the present invention chalcopyrite and other copper iron sulfide ore concentrates are reacted with sulfur vapor to form other copper iron sulfide materials. These new products which have an increased sulfur content are substantially more responsive to leaching than chalcopyrite and other non-sulfur treated copper iron sulfide minerals.

The reactor shown in Figures 1 and 2 can be used to treat copper iron sulfides in accordance with the present invention. Figure 1 is a vertical section view of a modified Herreshoff type furnace reactor 1. Heating elements 2 are used to heat the reactor and are located adjacent to the outer insulating fire brick wall 3. The ore concentrate is fed into the reactor via inlet star feeder 4 and conduit 5. Inside the stainless steel reaction chamber 6 are five stainless steel plates 7 (only the bottom plate is marked with the numeral 7 in Figure 1), each having a slot-type opening for continuous flow of the ore concentrate. On the center shaft 8 for each plate are mounted five stainless steel scraper blades 9, as shown in Figure 2. The ore concentrate is scraped horizontally across each plate 7 and drops vertically by gravity to the plate below, finally exiting the reaction chamber 6 as the reaction product through conduit 10 and exit star feeder 11.

Elemental sulfur which has been liquefied outside the reactor is fed through conduit 12 to sulfur flash pot 13 where it is vaporized. The vaporized sulfur is introduced into reaction chamber 6 through conduit 14. Excess sulfur vapor exits the reactor via conduits 10 and 15.

Nitrogen is introduced through conduit 16 and is used as a carrier for the sulfur vapor and in controlling the partial pressure of sulfur vapor. Additional nitrogen is introduced into conduits 5 and 10 at 17 and 18, respectively, to maintain a nitrogen atmosphere in the reaction chamber 6 and to aid in controlling the sulfur partial pressure.

The principal copper containing product (at least about 70% by weight) has been concluded to be x-bornite based upon the description of x-bornite found in an article by Yung and Kullerud entitled "Thermal Stability of Assemblages in the Cu-Fe-S System", Journal of Petrology, Vol. 7, Part 3, pp. 454-88 (1966). Pyrite as well as some bornite Cu_2FeS_4 and idaite Cu_3FeS_4 are also formed. The two principal products, pyrite and x-bornite, generally comprise at least about 85% by weight of the reaction product. Table I below presents x-ray diffraction pattern data for material produced by sulfidizing chalcopyrite ore concentrate in accordance with this invention as compared to the data presented for x-bornite in the Yund et al article and standard data for bornite, pyrite and other minerals.

TABLE I
Standard Data For:

Pattern Data of Sample		X-Bornite		Pyrite		Idaite		Bornite		SiO ₂ (Quartz)		MoS ₂		Chalcopyrite	
2θ	I	D	I/I max	D	I/I max	D	I/I max	D	I/I max	D	I/I max	D	I/I max	D	I/I max
14.48	30	6.11										6.15	100		
20.92	15	4.24								4.26	35				
26.68	60	3.34								3.343	100				
27.60	50	3.23													
27.98	40	3.19						3.18	60						
28.56	150	3.12	3.11	48	3.128	36	3.134	100							
29.40	45	30.4												3.03	100
31.84	20	2.808					2.818	80							
32.80	25	2.728							2.74	50					
33.10	260	2.704	2.699	43	2.709	84									
37.12	150	2.420			2.423	66									
40.80	110	2.210			2.212	52									
47.00	30	1.932							1.937	100					
47.50	210	1.912	1.910	100	1.916	40									
48.20	30	1.886					1.887	65							
56.32	150	1.632	1.630	21	1.633	100									
59.10	15	1.562	1.559	7	1.564	14									
61.72	30	1.502			1.502	20									
64.30	30	1.447			1.448	24									

2θ — angle of detection

D — interplanar spacing in Angstrom Units

I — intensity in counts per second

I/I max — relative intensity in per cent

Example.

The material for which x-ray diffraction data are presented in Table I was produced by treating chalcopyrite ore concentrate with sulfur vapor maintained at a partial pressure of 200 mm of Hg for 13 minutes. The reaction temperature was 471°C. and sulfur/copper molar ratio of the feed material to the reactor was 1.3. The chalcopyrite ore concentrate used in this example as well as in the other examples reported herein was obtained from Duval Corporation's Sierrita mine near Tuscon, Arizona. A wet chemical analysis of this ore concentrate showed 1.13% acid soluble copper, 2.48% non-chalcopyrite copper, 23.23% chalcopyrite copper, 28.1% iron and 30.3% sulfur.

With reference to the x-ray diffraction data presented in Table I, it can be seen that some of the x-bornite peaks overlap some of the pyrite peaks which prevents a positive identification of the material as either pyrite or x-bornite. For example, the peak at a 2θ value of 47.50° has a much higher intensity relative to the peak at the 2θ value of 56.32° than it has in a known pyrite sample. The peak at the 2θ value of 47.50° in the Table I sample is about 140% of the peak at the 2θ value of 56.32° , while in a known pyrite sample it is only about 40% of the peak at the 2θ value of 56.32° .

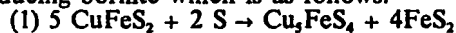
Comparative Example.

Consequently, to obtain a more positive identification of the x-bornite, a known sample of bornite was reacted with sulfur vapor under similar reaction conditions. The only different reaction condition was the use of a 1.0 sulfur/copper molar feed ratio. The x-ray diffraction data for the product material is presented in Table II and indicates, based on the data from the Yund et al article, that the material is x-bornite.

TABLE II

Pattern Data of Sample			Standard Data For:			
			X-Bornite		(Quartz)	
2θ	I	D	D	I/I max	D	I/I max
20.98	40	4.23			4.26	35
26.76	170	3.33			3.343	100
28.66	200	3.11	3.11	48		
33.16	180	2.699	2.699	43		
47.58	420	1.910	1.910	100		
56.38	90	1.630	1.630	21		
59.20	30	1.559	1.559	7		

The true relationship of x-bornite to bornite is not exactly clear, as is indicated in the Yung article. Yung and Kullerud suggests that x-bornite contains slightly more sulfur than stoichiometric bornite Cu_2FeS_4 . The reaction of sulfur with chalcopyrite to produce x-bornite is probably similar to the reaction producing bornite which is as follows:



During theoretical phase relation studies, Yung and Kullerud were able to produce x-bornite by annealing sulfur-rich synthetic bornites at a temperature below approximately 140°C . Although x-bornite occurs in some geological environments, there is no suggestion in the Yund article or other prior art of the means for producing x-bornite on a commercial basis as is disclosed herein.

The reaction temperature for producing x-bornite can range from the temperature at which sulfur vaporizes, 440°C. to 530°C. The optimum temperature for sulfidizing chalcopyrite ore concentrates has been found to be in the range from 460°C. to 500°C.

5 In treating chalcopyrite ore concentrates, partial pressures of sulfur above approximately 200 mm of Hg promote the reaction with chalcopyrite. Increasing the sulfur partial pressure from about 200 mm of Hg to about one atmosphere does not seem to affect the reaction one way or the other. Sufficient sulfur should be initially fed to the reaction vessel to maintain the partial pressure at 200 to 760 mm of Hg. It has been found that this can usually be accomplished by using a sulfur/copper molar feed ratio from about 1.2 to about 1.6. To keep the desired sulfur partial pressure additional sulfur is supplied during the reaction to provide for replacement of the reacted sulfur. Figure 3 shows the percent conversion of chalcopyrite as a function of temperature and sulfur partial pressure.

10 A minimum residence time (defined as the time the ore remains in the reactor) of about 6 minutes is necessary for obtaining a high conversion of chalcopyrite during the sulfidizing reaction at optimum conditions. This is shown by Figure 4. This graph in Figure 4 also indicates that an increase in the residence time has no significant effect in reducing the amount of residual chalcopyrite in the reaction product.

15 If a reaction product consisting primarily of x-bornite is kept at the reaction temperature under a nitrogen atmosphere for an additional period of time, a different product is formed which is primarily bornite. This can be seen from Table III which shows x-ray diffraction data for the final reaction product resulting from heating sulfidized chalcopyrite at 471°C. for 12 minutes in a nitrogen atmosphere.

25

TABLE III
Standard Data For:

Pattern Data of Sample		Bornite		Pyrite		X-Bornite		Idaite		SiO ₂ (Quartz)		MoS ₂		Chalcopyrite	
2θ	I	D	I/I max	D	I/I max	D	I/I max	D	I/I max	D	I/I max	D	I/I max	D	I/I max
14.50	10	6.10													
20.98	15	4.23													
21.84	10	4.07	4.08	10						4.26	35	6.15	100		
26.72	60	3.33								3.343	100				
27.04	20	3.29	3.31	40											
27.56	50	3.23													
27.98	50	3.19	3.18	60											
28.32	50	3.15													
28.58	100	3.12				3.128	36	3.11	48	3.134	100				
29.46	25	3.03												3.03	100
31.68	20	2.622													
31.98	15	2.796	2.80	20						2.818	80				
32.80	50	2.728	2.74	50						2.792	60				
33.06	195	2.707				2.709	84	2.699	43						
35.74	20	2.510	2.50	40											
37.12	100	2.420				2.423	66								
40.84	90	2.208				2.212	52								
47.00	90	1.932	1.937	100											
47.50	140	1.912				1.916	40	1.910	100						
55.74	20	1.648	1.652	30											
56.34	200	1.632				1.633	100	1.630	21						
59.06	25	1.563				1.564	14	1.559	7						
61.70	35	1.502				1.502	20								
64.32	35	1.447				1.448	24								

2θ — angle of detection

I — intensity in counts per second

D — interplanar spacing in Angstrom Units

I/I max — relative intensity in per cent

Under optimum reaction conditions the amount of residual chalcopyrite in the reaction product is approximately 1—3% by wet chemical analysis. To further reduce the residual chalcopyrite, the reaction product can be recycled through the reactor and treated as described above. However, the main product of such recycling is idaite instead of x-bornite. As will be discussed later, idaite is similar to

x-bornite in its responsiveness to leaching. Table IV presents x-ray diffraction data for the reaction product of recycling the initial reaction product at 471°C. for 13 minutes. The sulfur/copper molar feed ratio was 1.39 and the sulfur partial pressure was maintained at 208 mm of Hg.

TABLE IV
Standard Data For:

Pattern Data of Sample		Idaite		Pyrite		X-Bornite		SiO ₂ (Quartz)		Chalcopyrite		MoS ₂	
2θ	I	D	D	I/I max	D	I/I max	D	I/I max	D	I/I max	D	I/I max	D
14.52	35	6.10											
20.00	15	4.44											
20.96	15	4.23											
23.90	20	3.72											
26.68	35	3.34											
27.32	55	3.26											
27.62	40	3.23											
28.06	55	3.18											
28.54	230	3.12											
29.46	20	3.03											
31.74	160	2.817											
32.04	130	2.791											
33.14	220	2.701											
36.60	20	2.453											
37.16	125	2.417											
40.86	125	2.207											
42.52	20	2.124											
47.52	130	1.912											
48.20	155	1.886											
49.36	115	1.845											
56.34	205	1.632											
56.92	35	1.616											
59.04	80	1.563											
61.74	45	1.501											
64.36	55	1.446											

2θ — angle of detection

I — intensity in counts per second

D — interplanar spacing in Angstrom Units

I/I max — relative intensity in per cent

The sulfidizing of chalcopyrite and other copper iron sulfide minerals is especially adaptable to continuous processing techniques. The reaction time is relatively short and the reaction product can be easily handled and transported since it is in granular form.

In contrast to the vapor-phase reaction of the present invention, the liquid-phase reaction of the prior art, that is, heating a mixture of solid sulfur and copper iron sulfide ore concentrates to the point where the liquid phase sulfur is present either as a solid-liquid, liquid only or liquid-vapor phase, the resulting reaction product presents difficult material handling problems. Large pieces of product, which has been found to be mainly idaite, are formed, and frequently the product sticks to and fouls the walls of the reaction vessels. Consequently, before leaching, the liquid-phase reaction product must be ground to a fine particle size. In addition, due to the fouling of the reaction vessel the liquid-phase reaction presents difficulties for normal batch and continuous processing.

In the vapor-phase sulfidizing of chalcopyrite, the particle size of the products is actually less than that of the incoming chalcopyrite ore concentrate. For example, the mass mean diameter of the chalcopyrite ore concentrate particles was 0.091 mm with only 48 weight percent passing through a 200 mesh screen. After vapor-phase sulfidizing the chalcopyrite ore concentrate, the mass mean diameter of the resulting product particles was 0.068 mm with 87 weight percent passing through a 200 mesh screen.

The objective of the sulfidizing reaction is to produce a copper iron sulfide material from which the copper can be quickly leached in appreciable quantities by conventional leaching agents, such as sulfuric acid-oxygen solutions, sulfuric acid-ferric sulfate solutions, and ferric chloride and/or cupric chloride solutions, at relatively low pressures and temperatures.

A method for pressure leaching of chalcopyrite with sulfuric acid and oxygen is reported by Vizsolyi et al at page 52 of the November 1967 issue of the Journal of Metals. To obtain at least 98 percent solubilization of the chalcopyrite within three hours, the particles had to be ground to a size where 99.5% passed through 325 mesh screen and 50% stoichiometric excess of sulfuric acid was required. The oxygen partial pressure and temperature were maintained at 500 p.s.i. and 116°C. respectively.

In U.S. Patent No. 3,459,535, Vizsolyi et al described a process for leaching a covellite-pyrite material with oxygen and sulfuric acid at 90°C. and 70 p.s.i. of oxygen. The covellite-pyrite material was prepared by reacting sulfur with chalcopyrite in a batch reactor at 475°C. for 2 hours. Solid sulfur and chalcopyrite ore concentrate were inserted into the reactor and then heated to 475°C. The resulting material had to be broken up and ground before leaching to a particle size of substantially 100% through 325 mesh or less. During the leaching step, five hours of residence time was required to obtain copper extractions greater than 98.5 weight percent, and under these conditions 53 weight percent of the iron from the pyrite was leached.

In the present invention over 98.5% of the copper can be solubilized in as little as two hours by leaching the sulfidized copper iron sulfides with sulfuric acid and oxygen. For one set of examples, the copper iron sulfides from the vapour phase reactor were not ground as in prior art processes but were only screened to remove the plus 100 mesh size particles and then pressure leached in an autoclave using only one stage. Table V below shows: (A) the composition of the copper iron sulfides resulting from the vapor phase sulfidizing of chalcopyrite ore concentrates; (B) results of leaching tests on sulfidized ore; (C) results of leaching tests on chalcopyrite ore; and (D) reaction conditions for these leaching tests.

TABLE V
CONDITIONS AND RESULTS FOR PRESSURE LEACHING
USING SULFURIC ACID AND OXYGEN

A.

COMPOSITIONS OF THE COPPER IRON SULFIDES
(SULFIDIZED ORE)

Sulfidized Ore Sample	Wet Chemical Analyses (Wt %)			X-ray Diffraction Analysis
	Cu	Fe	S	
No. 1	24.71	24.19	36.19	2-3% chalcopryrite; 20-25% x-bornite remainder is pyrite
No. 2	24.71	24.90	36.10	4-5% chalcopryrite; 3% idaite; 20-22% x-bornite remainder is pyrite

B.

LEACHING TESTS ON SULFIDIZED ORE

Test No.	Sulfidized Ore Sample	Residence Time (hrs)	Wt % Solubilized		
			Cu	Fe	S
1	No. 1	2	98.5	27.0	0.2
2	No. 1	2.5	98.8	27.0	1.3
3	No. 2	2	99.0	37.1	8.0

C.

LEACHING TESTS ON CHALCOPYRITE ORE

Test No.	Residence Time (hrs)	Wt % Solubilized		
		Cu	Fe	S
4	2	57.1	24.1	0
5	2	55.4	31.3	0

Note: For Test No. 4, the chalcopryrite was dried at 475°C. in a nitrogen atmosphere prior to leaching.

D.

REACTION CONDITIONS

Temperature: 70°C.
Oxygen Partial Pressure: 90 p.s.i.
Stirrer Speed: 1500 rpm
Wt % of sulfuric acid in leach liquor: 13.0%
Grams of leach liquor per gram of sulfidized ore: 3.76

It can be seen from Table V that only 55—57% copper is solubilized when leaching chalcopyrite ore as compared to 98.5—99.0% of solubilization when leaching sulfidized ore. Moreover, only 27—37% of the iron in the sulfidized ore was solubilized.

5 The data in Table VI show the advantage of leaching x-bornite or idaite over native bornite or covellite ore. All the leaching tests were made at an oxygen partial pressure of 70 p.s.i. and 105°C. using about 13.0 wt. % sulfuric acid and 3.7 grams of acidic solution per gram of ore material. Stirrer speed was 1500 rpm and particle size of the ore material was minus 200 plus 325 mesh. Table VI and Figure 10 5 show the results of these leaching tests and illustrate the significant difference in the leaching characteristics of the different materials. The sulfidized materials, idaite and x-bornite, are considerably more susceptible to acid leaching than the other materials. 10

TABLE VI
CONDITIONS AND RESULTS FOR PRESSURE LEACHING USING SULFURIC ACID AND OXYGEN

Test No.	Material Leached	Residence Time (hrs)	Initial Wt % H_2SO_4	Wt % Solubilized			Chemical Analysis of Spent Residue			
				Cu	Fe	S	Acid Soluble Copper	Copper as Chalcocite	Copper as Chalcocopyrite	
1	x-bornite (1)	1	12.98	97.0	30.6	11.6	.51	.43	.30	
2	x-bornite (1)	1.5	12.98	97.5	27.5	10.2	.45	.39	.25	
3	x-bornite (1)	2	12.98	98.5	37.4	11.7	.34	.14	.15	
4	Native Covellite	1	12.98	58.0	19.6	0				
5	Native Covellite	1.5	13.13	67.0	24.9	0				
6	Native Covellite	2	13.13	79.2	26.8	0				
7	Native Bornite	1	13.13	79.2	58.7	0				
8	Native Bornite	1.5	13.13	87.0	72.0	0				
9	Native Bornite	2	13.13	92.6	78.1	0				
10	Idaite (2)	1.5	12.97	93.8	20.9	3.2				
11	Idaite (2)	2	12.97	94.3	21.0	0				
12	Idaite (2)	2	13.13	95.9	24.1	5.8	.39	1.09	.21	
13	Idaite (2)	1.5	13.13	89.8	18.2	13.1	.23	3.52	.34	
14	Idaite (2)	2.5	13.13	97.0	33.5	11.1	.34	.73	.21	

(1) Composition by x-ray diffraction is mainly x-bornite and pyrite with about 4% chalcocopyrite and some idaite.

(2) Composition by x-ray diffraction is mainly idaite and pyrite with about 1% chalcocopyrite and some x-bornite and bornite (vapor-phase preparation).

5 In attempting to maximize the copper recovery, it was found through the use
of microphotographs that pyrite crystals are imbedded at random in the crystals of
the sulfidized copper iron sulfides during the vapor-phase sulfidizing reaction. In
some cases 2—3% of the total copper is entrapped, in the form of copper iron
sulfide crystals, by the pyrite crystals and is thus shielded from the leaching
solution. Accordingly, this invention provides a method for leaching the copper
entrapped by the pyrite crystals. 5

10 It was unexpectedly discovered that by grinding the residue from a one-stage
pressure leach reaction, during which most (at least about 80%) of the copper was
solubilized, the pyrite crystals can be "cracked" away, thereby exposing the
remaining copper iron sulfides to the leaching agents. By this method it is possible
to solubilize substantially all or in excess of about 99% of the copper in the copper
iron sulfides produced by the use of the vapor phase sulfidizing reaction. It has
been found that extensive grinding of the sulfidized ore prior to any leaching does
not materially enhance the solubilization of the copper. 15

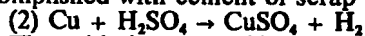
20 To illustrate this method for maximizing copper recovery, copper iron sulfide-
pyrite products from the vapor phase sulfidizing reaction were screened to obtain
a particle size of 100 percent through 100 mesh. This material was pressure leached
in an autoclave with sulfuric acid and oxygen. The washed residue was ground to
less than 325 mesh or less than 200 mesh to "crack" away the pyrite crystals and
releached with fresh leaching solution. The conditions and results for both stages
of these tests are given in Table VII. 20

TABLE VII
CONDITIONS AND RESULTS FOR THE TWO-STAGE LEACHING TESTS

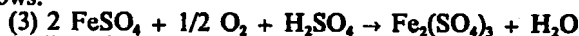
Test No.	Stage	Material Leached	Size of Material (mesh size)	Total Press. p.s.i.	Residence Time Hr.	Gms H_2SO_4 per Gms Cu	Wt % Solubilized Across One Stage			Wt % Solubilized Across Both Stages		
							Cu	Fe	S	Cu	Fe	S
1	1	x-bornite	-100	88	2	2.0	96.6	48.2	23.6			
	2	Residue Stage 1	-325	88	1	59.5	92.0	39.9	24.5	99.7	68.8	42.3
2	1	x-bornite	-100	88	3	2.0	82.7	48.7	24.8			
	2	Residue Stage 1	-325	88	2	11.8	94.7	47.1	29.0	99.1	72.9	46.6
3	1	x-bornite	-100	88	3	2.0	96.1	55.3	29.4			
	2	Residue Stage 1	-325	88	1	29.7	87.2	34.5	17.5	99.5	70.7	41.7
4	1	x-bornite	-100	68	2	2.0	93.7	44.5	24.6			
	2	Residue Stage 1	-325	68	2	32.3	91.5	44.8	30.8	99.5	69.4	47.9
5	1	x-bornite	-100	68	1	2.0	87.2	28.8	5.9			
	2	Residue Stage 1	-200	68	1	15.9	67.6	23.4	16.3	95.8	46.2	21.3
6	1	x-bornite	-100	88	1	2.0	89.5	35.4	8.9			
	2	Residue Stage 1	-200	88	1	19.3	75.7	27.9	15.4	97.4	53.9	23.0
7	1	x-bornite	-100	88	2	2.0	95.8	49.8	22.1			
	2	Residue Stage 1	-200	88	1	49.2	78.2	29.2	15.3	99.1	64.4	34.0
8	1	x-bornite	-325	88	2	2.0	95.7	37.7	15.0			
	2	Residue Stage 1	-325	68	2	47.7	94.0	55.7	26.7	99.7	72.4	37.6

The resulting pregnant liquor from the pressure leach reaction contains an appreciable amount of iron which must be removed before the copper sulfate solution can be treated by electrolysis to produce metallic copper. Excess iron in the electrolytic cell reduces the cathode efficiency and can contribute to contamination of the copper.

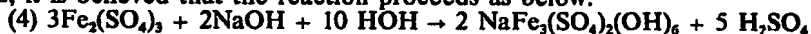
It has been found that the iron can be removed by precipitating it as a jarositic iron oxide-sulfate. The ratio of sulfate ions to iron in the combined precipitate has been found to be essentially that of the compound jarosite. It is precipitated from an acid solution at pH values of 1.5 and above. Since the pregnant liquor from the leach reaction contains excess sulfuric acid, the pH values range from 0.5 to 1.0. Thus, before jarosite can be precipitated the excess sulfuric acid must be neutralized. In the present invention the neutralization of the sulfuric acid can be accomplished with cement or scrap copper according to the following equation:



The oxidation state of iron in jarosite is +3, thus any ferrous ions in the liquor must be oxidized to ferric ions. This is accomplished by oxidation with oxygen as follows:



Sodium ions for the jarosite formation can be supplied by such sodium compounds as sodium hydroxide or sodium carbonate. When sodium hydroxide is used, it is believed that the reaction proceeds as below:



The reactions above can be carried out in one reactor, or the cement copper and the sodium hydroxide can be added prior to the oxidation step. The reaction has been carried out in a standard autoclave in which the pressure leach tests were conducted. The pregnant liquor, cement copper, and sodium hydroxide were placed in the autoclave at the same time. The temperature was increased and oxygen was then applied under pressure.

High temperature was used because it produced a more easily filterable precipitate. The oxidation rate of the ferrous ions to ferric ions increased with the use of high pressure.

A number of runs were made during which about 80 percent of the iron in the pregnant liquor was removed. Very little copper remained in the residue with the iron. For these tests, enough cement copper was added to the liquor to bring the pH up to 1.5—2.0 and enough sodium hydroxide was added to satisfy the reaction of equation (4). The conditions for carrying out these tests were as follows:

Temperature:	115°C.
Contact Time:	2 hrs.
Partial Pressure of Oxygen:	70 p.s.i.
Total Pressure:	95 p.s.i.
Stirrer Speed:	1,500 rpm

Table VIII below contains the conditions and results of these tests.

TABLE VIII
CONDITIONS AND RESULTS FOR IRON REMOVAL TESTS

Test No.	Gms. of Liquid Feed	Liquid Feed Wt. %			Gms. of Cement Copper	Gms. of 100% NaOH	Liquid Product Wt. %				Spent Residue Wt. %		
		Cu	Fe	S			Cu	Fe	S	pH	Cu	Fe	S
1	300	5.65	1.40	4.29	9.0	0.3	4.43	.14	1.89	1.5	1.4	45.2	—
2	300	6.20	1.04	3.60	2.0	2.0	3.86	.11	1.69	1.45	1.6	39.6	—
3	300	5.89	1.89	4.27	3.0	1.1	5.89	.16	3.2	1.1	0.9	28.1	—
4	600	5.75	1.96	—	9.0	2.0	6.32	.29	—	1.1	1.0	30.9	—
5	600	5.65	1.72	4.04	10.75	2.2	7.69	.29	3.72	—	1.2	26.3	9.23
6	600	5.65	1.12	3.51	10.0	0	4.47	.16	—	1.5	2.6	25.3	—
7	1263	9.03	1.79	5.87	30	4.8	4.39	.14	2.08	—	1.3	17.1	4.4
8	300	6.94	1.85	5.58	0	15	6.37	.24	4.89	—	3.4	29.3	12.9

Analysis of cement copper used in wt. %:

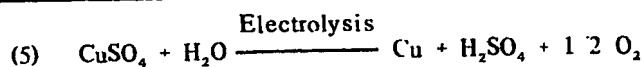
Cu — 83.6%

Fe — 8.0%

S — 0.4%

After about 80% of the iron has been removed from the pregnant liquor, the solution contains approximately 6—8% copper, 0.2—0.4% iron, and 1—3% free sulfuric acid. The copper in this solution can be recovered in metallic form by conventional electrowinning methods. Equation (5) sets forth the reaction in the electrolytic cell:

5



About 60% of the copper in the copper sulfate solution is removed during electrolysis at the following conditions:

	Temperature:	30—50°C.	
5	Contact Time:	14—21 hrs.	5
	Voltage:	1.6—2.5 volts	
	Current Density:	7 to 25 (Amps/Sq. Ft.)	
	Current Efficiency:	About 85%	

10 IX: The conditions and results of typical electrowinning tests are shown in Table 10

TABLE IX

RESULTS AND CONDITIONS FOR ELECTROWINNING TESTS

Test No.	1	2	3
<u>Conditions:</u>			
Temperature (°C.):	30	30	30
Voltage (Volts):	2.0	2.0	2.3
Current Density (Amps./sq. ft.):	7.0	7.0	25
Liquid Feed (wt. %):			
Cu	3.5	3.5	3.4
Fe	0.13	0.4	0.6
S	4.3	4.3	4.5
Contact Time (hrs.):	21	21	9
<u>Results:</u>			
Current Efficiency (%)	88	71	78
% Copper Removed	61	51	54
Rate of Copper Depletion (gms/hr):	1.2	0.97	2.3

15 Another advantage of the above-described method is that the purification of cement or scrap copper can be incorporated into the overall process. As was discussed previously, cement or scrap copper is added to the system to neutralize excess sulfuric acid in the iron removal step. 15

One embodiment of the process according to the present invention wherein sulfuric acid is used as the leaching agent is shown by the flow diagram in Figure 6. In treating chalcopyrite ore concentrates, the ore concentrates are added to sulfidizing reactor 101 through line 102. Molten sulfur is introduced into reactor 101 through line 103 wherein it is vaporized before being mixed with the ore concentrates. The vaporized sulfur is preferably maintained at a partial pressure of 20

at least 200 mm of Hg. In the reactor the ore concentrates are sulfidized in as little as six minutes at a temperature of about 470°C., thereby converting most of the chalcopyrite to x-bornite and pyrite. Excess sulfur is discharged through line 104.

The sulfidized ore from reactor 101 is then passed through line 105 to primary leach stage 106, into which is also passed sulfuric acid solution through line 107 and oxygen sufficient to maintain a partial pressure of about 90 p.s.i. through line 108. The acid oxidation leach solution at a temperature of about 105°C. solubilizes most of the copper in the ore in about two hours.

The leach slurry from the primary leach stage is then transported through line 109 to primary separation device 110. In this device the solids consisting primarily of a small amount of unreacted copper iron sulfides, elemental sulfur and insoluble residue are separated from the solution containing copper sulfate, ferrous sulfate and unreacted sulfuric acid. The solids are transported through line 111 to grinding stage 112 and the solution goes to iron removal stage 114 through line 113.

In the grinding stage the solids are further ground by use of conventional size reduction equipment to at least about less than 200 mesh (U.S. standard sieve). The ground solids are then transported to secondary leach stage 116 through line 115.

To solubilize essentially all the remaining copper in the copper iron sulfides, oxygen is added to the secondary leach stage through line 117 and regenerated sulfuric acid solution is added through line 118. The reaction conditions are essentially the same as those in the primary leach stage. The resulting slurry is then transported to secondary separation device 120 through line 119.

In device 120 conventional separation means are used to separate the solution containing excess sulfuric acid, ferrous sulfate and copper sulfate from the solid material consisting primarily of elemental sulfur and insoluble residue which is discharged through line 121. If desired the elemental sulfur can be separated from the residue by means known to those skilled in the art. The solution is discharged from device 120 through line 122 and is combined with the regenerated sulfuric acid solution that is added to the primary leach stage through line 107.

In iron removal stage 114 the pregnant liquor containing copper sulfate, ferrous sulfate and excess sulfuric acid is first treated to neutralize the excess sulfuric acid by the addition of cement copper through line 123. Oxygen sufficient to maintain a partial pressure of about 70 p.s.i. is added through line 124 to oxidize the ferrous ions to ferric ions and sodium hydroxide is added through line 125 to precipitate the ferric iron as jarositic iron oxide-sulfate. The preferred reaction temperature is 115°C. and the normal contact time is about 1—2 hours.

The slurry from iron removal stage 114 is transported through line 126 to iron separation device 127 wherein the jarositic material is separated from the solution containing primarily copper sulfate and some ferric sulfate. The jarositic material is discharged through line 128 and the solution is transported through line 129 to electrolytic cells 130. The jarostic material may alternatively be recycled to either the primary or the secondary leach stage for the removal of any copper therein. In such case the jarositic precipitate would be removed from the process with the insoluble residue.

The solution in cells 130 is electrolyzed to produce metallic copper and to regenerate sulfuric acid. Metallic copper is removed at 131 and the regenerated sulfuric acid solution which is used in both the secondary and primary leach stages is discharged through line 107.

The x-bornite and idaite prepared by the process according to the present invention offers a considerable advantage in the use of ferric chloride and/or cupric chloride as the leaching agent. Considerably more copper can be leached from x-bornite or idaite than chalcopyrite during a given period of time. Table X contains conditions and results for atmospheric pressure leaching of x-bornite and chalcopyrite using ferric chloride and cupric chloride, along with sodium chloride which acts to keep cuprous chloride in solution and is believed to aid the reaction.

TABLE X

CONDITIONS AND RESULTS FOR ATMOSPHERIC PRESSURE LEACHING
USING FERRIC CHLORIDE AND CUPRIC CHLORIDE

A.

REACTION CONDITIONS

Temperature: about 110°C.

Pressure: Atmospheric

Grams FeCl_3 /Grams Sulfidized Ore: 1

Grams $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ /Grams Sulfidized Ore: 0.2

Grams H_2O /Grams Sulfidized Ore: 2.8

Sulfidized Ore Composition: By wet chemical analysis —
26.23% Cu, 25.14% Fe and 30.00% S.
By x-ray diffraction analysis, 4% chalcopyrite,
about 2% bornite, about 4% idaite, 21–22%
x-bornite, with the remainder being pyrite.

B.

LEACHING TESTS ON SULFIDIZED ORE

Test No.	Gms NaCl	Reaction Time (hrs)	Wt % Solubilized		Material Balance (Wt %)	
	Gms Ore		Cu	Fe	Cu	Fe
1	0.8	0.5	98.7	14.5	105.6	102.7
2	0.8	0.25	98.8	17.2	101.8	95.5
3	1.0	0.25	99.4	26.2	89.4	92.4

Note: The residue cake was washed by re-slurrying with dilute hydrochloric acid.

C.

LEACHING TESTS ON CHALCOPYRITE ORE

Test No.	Gms NaCl	Reaction Time (hrs)	Wt % Solubilized		Material Balance (Wt %)	
	Gms Ore		Cu	Fe	Cu	Fe
4	1.0	0.25	51.3	44.2	108.5	93.8
5	0.8	0.25	51.6	46.5	108.8	99.4

Note from Table X the fast rate of the dissolution reaction with x-bornite. Within 15 minutes more than 98.5% of the copper was solubilized. Under the same conditions only 51% of the copper in the chalcopyrite was leached.

From the foregoing detailed description, it can be seen that the present invention provides a means for utilizing hydrometallurgical processes for the recovery of metallic copper from copper iron sulfide ore concentrates whereby conventional pyrometallurgical processes can be replaced, thus eliminating the air pollution associated with the processing of such ore concentrates. The invention also resides in the development of a process for treating copper iron sulfide ore concentrates which will make the copper iron sulfides, especially chalcopyrite, more responsive to leaching in hydrometallurgical processes.

WHAT WE CLAIM IS:—

1. A method of processing copper iron sulfide ore concentrates for the hydrometallurgical production of metallic copper wherein the ore concentrates are leached to solubilize the copper, comprising the step of making the copper iron sulfides in the ore concentrates more responsive to the leaching by reacting sulfur vapor having a partial pressure of at least 200 mm Hg with the ore concentrates at a temperature of from 440°C. to 530°C. for a period of at least 6 minutes.

2. The method according to claim 1 wherein the ore concentrates consist primarily of chalcopyrite ore concentrates and said ore concentrates are leached with a chloride solution.

3. The method according to claim 2, wherein the chloride leaching solution contains ferric chloride and cupric chloride.

4. The method according to claim 1 wherein the ore concentrates consist primarily of chalcopyrite ore concentrates and said ore concentrates are leached with a sulfate solution.

5. The method according to claim 4, wherein the sulfate leaching solution contains sulfuric acid and oxygen.

6. The method according to any one of claims 1 to 5, wherein the reaction temperature is in the range from 460°C. to 500°C.

7. A method of processing copper iron sulfide ore concentrates for the hydrometallurgical production of metallic copper, comprising the steps of solubilizing substantially all of the copper in the copper iron sulfides by:

(a) reacting sulfur vapor having a partial pressure of at least 200 mm Hg with the ore concentrates at a temperature of from 440°C. to 530°C. for a period of at least 6 minutes to form a reaction product consisting principally of copper containing material and pyrite;

(b) leaching the reaction product from step (a) to solubilize most of the copper in the reaction product;

(c) grinding the solid residue from step (b) to a particle size of less than 200 mesh (U.S. standard sieve); and

(d) leaching the ground residue from step (c) to solubilize substantially all the remaining copper in the reaction product.

8. The method according to claim 7, wherein the leaching in both steps (b) and (d) is performed with sulfuric acid solution under oxidizing conditions.

9. The method according to claim 7 or 8, wherein the ore concentrates consist primarily of chalcopyrite or bornite ore concentrates.

10. The method according to claim 7, wherein the leaching is performed with a ferric chloride-cupric chloride and sodium chloride solution.

11. The method according to any one of claims 7 to 10 wherein the solution containing the solubilized copper is reacted with cement copper to raise the pH of the solution to at least 1.5, including the steps of: (e) oxidizing the solution of pH at least 1.5 containing the solubilized copper to precipitate iron from the solution by the addition of oxygen and sodium carbonate or sodium hydroxide, said oxidation being performed at a temperature of at least 115°C. and at an oxygen partial pressure of 70 p.s.i. to precipitate the iron in the form of jarositic iron oxide-sulfate; and (f) electrolyzing the solution from which the iron has been precipitated to produce metallic copper and to regenerate sulfuric acid solution for reuse in the leaching steps.

12. The method according to claim 7, wherein the sulfur vapor reacted with the ore concentrates in step (a) is maintained at a partial pressure of 200 mm to 760 mm of Hg and the reaction temperature for step (a) is in the range from 460°C. to 500°C.

13. The method according to claim 11, wherein only the solution containing the solubilized copper from step (b) is oxidized in step (e) and the solution

containing the solubilized copper from step (d) is recycled along the regenerated sulfuric acid solution from step (f) to step (b).

5 14. The method according to claim 7, wherein the temperature of step (a) is from 460°C. to 500°C. to form a granular reaction product, wherein leaching from steps (b) and (d) take place with a sulfuric acid solution under oxidizing conditions to form slurries containing sulfur, solids, excess sulfuric acid, copper sulfate, and ferrous sulfate, and including the steps of:

10 (e) separating the sulfur and the solids in the slurry of step (b) from the solution containing the copper sulfate, ferrous sulphate and excess sulfuric acid;

(f) separating the sulfur and solids in the slurry of step (d) from the solution containing the copper sulfate, ferrous sulfate and excess sulfuric acid;

(g) reacting cement copper with the solution of step (e) to raise the pH of the solution to at least 1.5;

15 (h) reacting the solution of step (g) with sodium hydroxide and oxygen at a partial pressure of at least 70 p.s.i. (g) at a temperature of at least 115°C to precipitate iron in the form of jarositic iron oxide-sulfate;

(i) electrolyzing the solution from which the iron has been precipitated to produce metallic copper and to regenerate sulfuric acid solution; and

20 (j) recycling the sulfuric acid solution of step (i) to step (d) and along with the solution of step (f) to step (b) for use in further leaching.

15. A method of processing copper iron sulfide ore concentrates for the hydrometallurgical production of metallic copper substantially as herein described in the Example set forth in the specification.

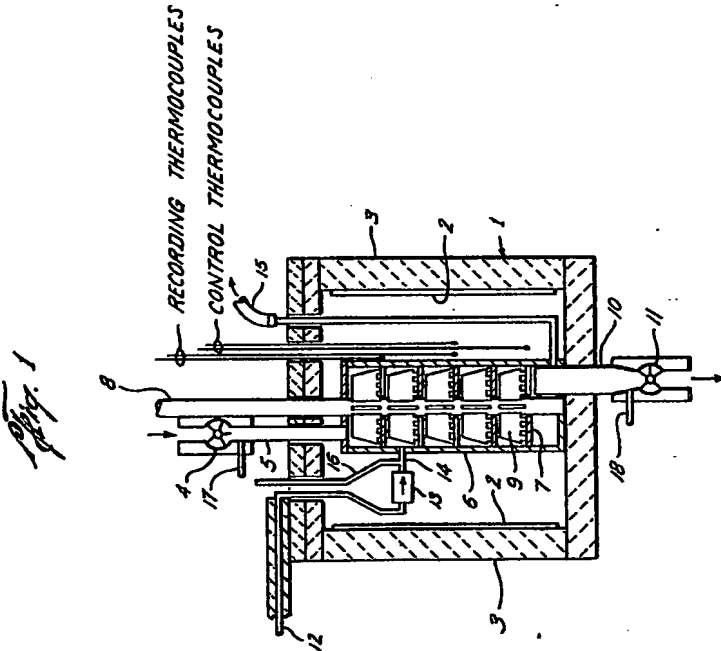
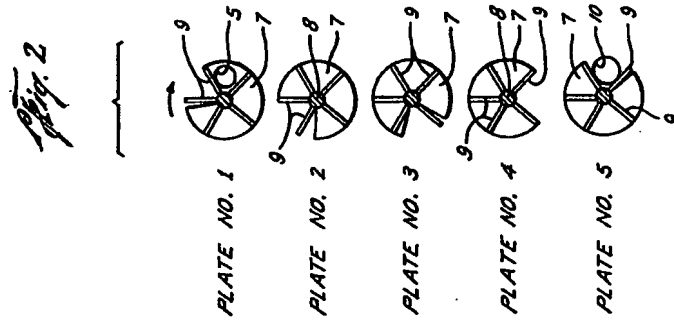
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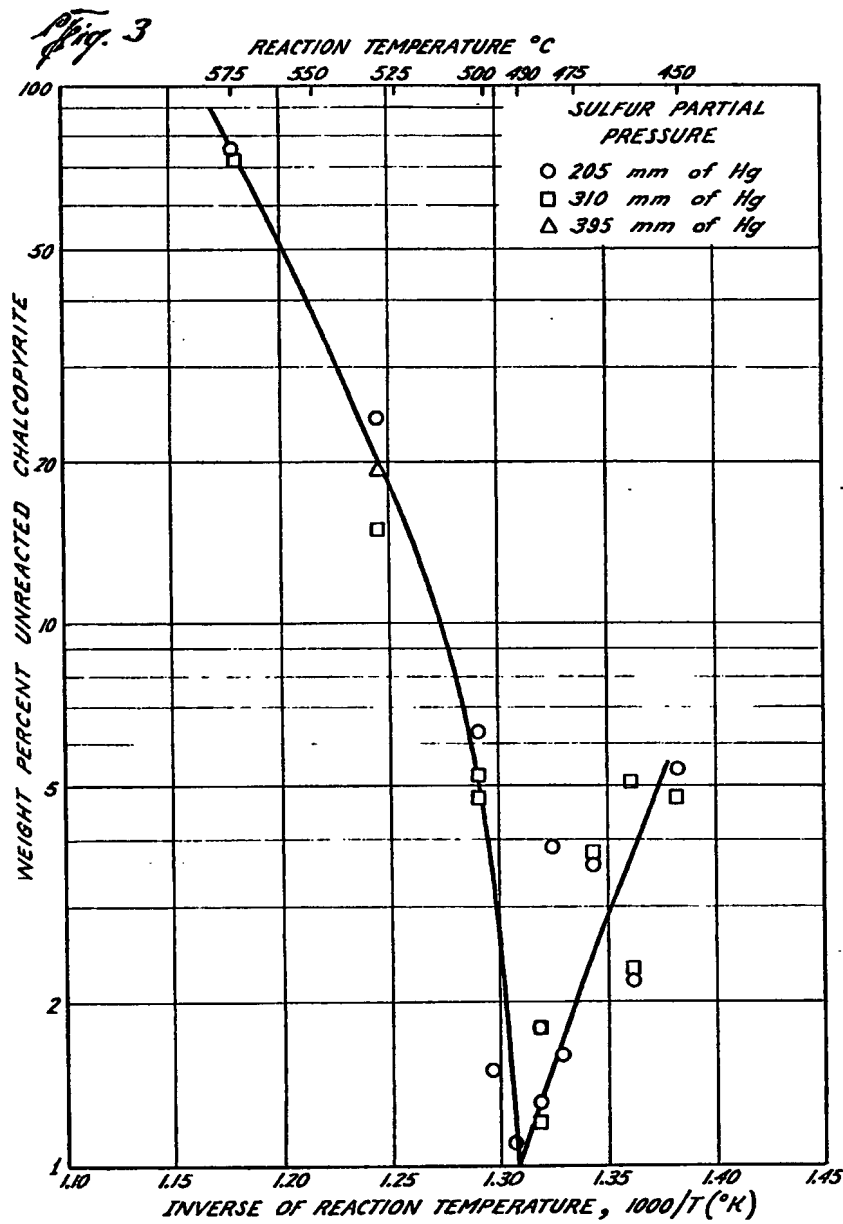
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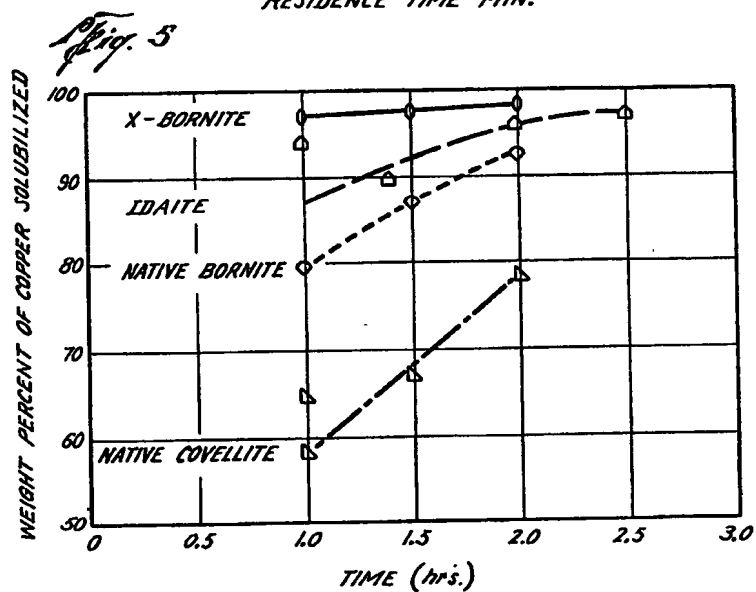
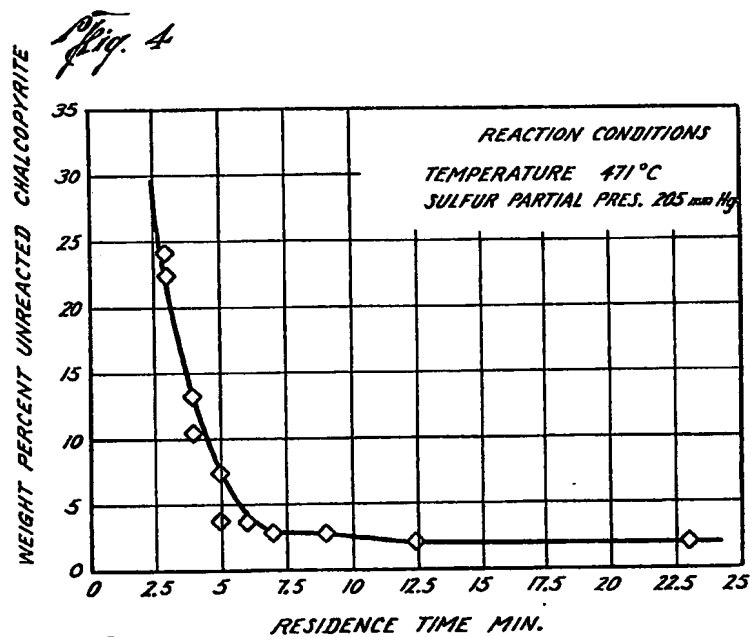
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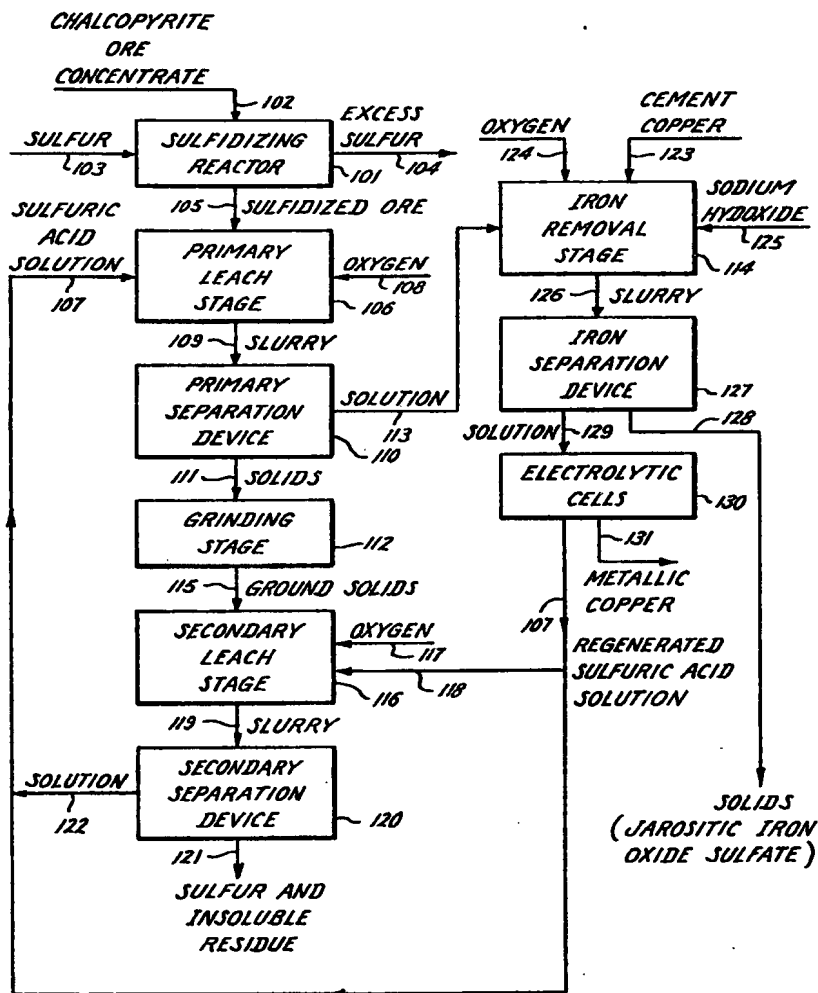
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Sheet 3



*Fig. 6*